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Notes

Internal Pressure & Free Volume of Potassium Chloride Solutions in Water-Dimethylformamide Mixtures

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Internal pressure and free volume have been calculated for potassium chloride solutions in water-DMF mixtures from ultrasonic velocity measurements at different concentrations and temperatures. For any given solution, at a given concentration, variation of internal pressure and free volume obeys the equation $\pi_i V_f^x = K$ in conformity with the results reported by Suryanarayana and Kuppusami [*J Accous Soc India*, **8** (1980) 29; **9** (1981) 6].

Whatever be the model chosen for the liquid state, the cohesive forces are of primary importance. Though the origin of these cohesive forces is known, all theories of liquids have failed to assess correctly these forces in totality in a simple and elegant way. However, one can estimate their magnitude from thermodynamic considerations. Such an estimate is provided by the internal pressure. In this note we have estimated the internal pressure and free volume of solutions of potassium chloride in DMF-water mixtures.

Dimethylformamide (Baker analysed) after drying over anhydrous potassium carbonate (24 hr), was purified by vacuum distillation over CaO. Doubly distilled water was used in the preparation of potassium chloride solutions.

Solutions of KCl at different concentrations in DMF-water (20:80 v/v) are prepared on molal scale. Solutions were also prepared in DMF-water (40:60 v/v).

Measurement of ultrasonic velocity

Ultrasonic interferometer, model M-77 (Mittal Enterprises, New Delhi) was used for measuring ultrasonic velocities of solutions of KCl at different temperatures: 30°, 35°, 40° and 45° ± 0.05°C.

Density

The densities of the solutions were measured at these temperatures using a specific gravity bottle of 20ml capacity.

Viscosity

The viscosities of the solutions at these temperatures were obtained using Oswald's viscometer.

Calculation of free volume and internal pressure of KCl solutions

Having measured the required parameters u, ρ and η of the solutions, the free volume, V_f and the internal pressure (π_i) were computed from Eqs (1) and (2) respectively[2,3].

$$V_f = \left[\frac{u M_{eff}}{K\eta}\right]^{3/2} \quad \ldots (1)$$

$$\pi_i = \alpha RT \left[\frac{K\eta}{u}\right]^{1/2} \frac{\rho^{2/3}}{M_{eff}^{7/6}} \quad \ldots (2)$$

where ρ = density, u = ultrasonic velocity, η = viscosity, M_{eff} = effective molecular weight of the me-

Table 1—Free Volume and Internal Pressure of Potassium Chloride Solutions in 20% and 40% DMF-Water Mixtures

KCl (*m*)	$V_f \times 10^2$ ml				π_i (atm)			
	30°	35°	40°	45°	30°	35°	40°	45°
				DMF-Water (20:80%)				
0	1.682	2.089	2.444	2.892	25513	24112	23212	22259
0.25	1.654	2.059	2.441	2.942	25649	24194	23191	22086
0.50	1.782	2.203	2.546	3.036	24992	23625	22843	21846
0.75	1.893	2.290	2.680	3.198	24454	23298	22426	21443
1.0	1.811	2.239	2.590	3.055	24776	23444	22646	21779
				DMF-Water (40:60%)				
0	1.378	1.742	2.096	2.530	23946	22468	21406	20385
0.25	1.338	1.678	2.004	2.402	24174	22740	21725	20735
0.50	1.389	1.765	2.074	2.514	23869	22355	21467	20408
0.75	1.388	1.759	2.114	2.553	23848	22322	21314	20293
1.0	1.429	1.803	2.113	2.544	23604	22159	21243	20298

Table 2—Values of Arbitrary Constants *a*, *b*, *c* and *d* of Eqs (3) and (4)

KCl (*m*)	$a \times 10^{-5}$	$b \times 10^{3}$	$c \times 10^{10}$	$d \times 10^{3}$
		DMF-Water (20:80%)		
0.25	5.262	9.971	1.463	38.392
0.50	3.785	8.785	3.769	35.522
0.75	3.476	8.760	4.746	34.957
1.0	2.785	7.986	3.545	32.641
		DMF-Water (40:60%)		
0.25	5.364	10.230	0.979	39.008
0.50	5.651	10.444	0.861	39.553
0.75	6.217	10.762	0.589	40.627
1.0	4.794	10.060	1.246	38.451

dium given by $\Sigma M_i x_i$ where M_i and x_i are the molecular weight and the molfraction of the individual constituents, respectively and α, the packing factor in liquids being equal to 2 for cubic packing. The experimental errors in the determination of V_f and π_i were respectively ±0.15% and 0.5%.

The values of V_f and π_i for KCl solutions in 20% and 40% (v/v) DMF-water mixtures are given in Table 1. It is observed that in pure aqueous solutions[4] both potassium and chloride ions are contributing to a fall in the internal pressure while in the case of DMF-water mixtures with a progressive increase in DMF content more and more K^+ ions are solvated heavily and only anions are left comparatively less solvated. Hence, though there is, in general, a trend of progressive fall in internal pressure with the increase in KCl concentration, a progressive increase in DMF immobilises the effect of K^+ ions and what is observed is only due to the concentration of chloride ions.

At all the concentrations of KCl, increase in temperature decreases the internal pressure and increases the free volume[5]. The plots of both V_f and π_i versus temperature are slightly non-linear, but the trend is the same in all the cases.

The variations of internal pressure and free volume with temperature at any given concentration can be expressed by Eqs (3) and (4) respectively.

$$\pi_i = a \exp(-bT) \qquad \ldots (3)$$

$$V_f = c \exp(dT) \qquad \ldots (4)$$

where *a*, *b*, *c* and *d* are arbitrary constants dependent on concentration (Table 2).

The plots of $\log \pi_i$ versus $\log V_f$ for given concentrations at different temperatures are linear and parallel satisfying the linear Eq. (5) propased by Suryanarayana and co-workers[4,5],

$$\pi_i V_f^x = K \qquad \ldots (5)$$

In Eq (5) *K* is a constant and x_{rms} value is computed to be 0.256 ± 0.007 and K_{rms} value is 1454 ± 185. *K*-values vary considerably between 20% DMF and 40% DMF and do not have much of a significance, in conformity with the results reported by Suryanarayana and Kuppusami[4,5]. *x* was found to be 0.288 in aqueous solutions.

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